Co-extraction of Iron and Sulfate by Bis(2,4,4-trimethylpentyl)phosphinic Acid, CYANEX®272

Co-extraction of iron and sulfate by CYANEX®272

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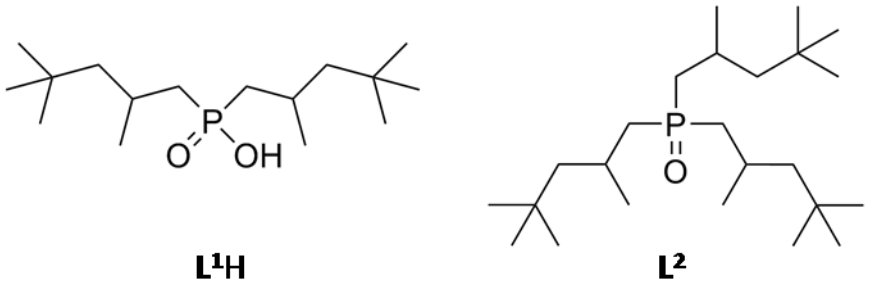
Abstract

The mode of action of iron(III) uptake from sulphate solutions by the commercial extractant CYANEX®272, bis(2,4,4-trimethylpentyl)phosphinic acid, has been studied using conventional solvent extraction methods, together with $^{31}P\{^{1}H\}$ NMR spectroscopy, electrospray-ionisation mass spectrometry and DFT calculations that have not previously been used to analyse the content of the ISOPAR M water-immiscible phase. The maximum Fe-loading recorded was 177% of the theoretical maximum, based on the formation of an Fe(III) complex $[Fe(L)_3]$ with a 1:3 molar ratio of Fe to phosphinate (L). Inductively-coupled plasma optical emission spectroscopy (ICP-OES) indicates that sulfate or hydrogen sulfate ions are co-extracted in a 1:2 molar ratio with iron across the whole of the Fe-loading range, which helps to account for the loadings being greater than 100% of the theoretical value. $^{31}P\{^{1}H\}$ NMR spectroscopy indicates that the limiting factor in Fe-loading is the availability of uncomplexed CYANEX®272 (sulfate is present in large excess). In contrast to the behaviour of Co(II) and Zn(II) extraction by CYANEX®272, there is no evidence for the formation of polymeric Fe(III) complexes and highly viscous solutions at high metal loadings. The identity of the extracted species is likely to be a polynuclear Fe(III) sulphate complex.

Keywords: CYANEX®272; Iron(III) extraction; solvent extraction.

1. Introduction

This paper considers the mechanism of uptake of Fe(III) from sulfate streams by the commercial organophosphorus extractant CYANEX®272, which consists predominantly of bis(2,4,4-trimethylpentyl)phosphinic acid ($\mathbf{L^1}$H, see Figure 1) along with small quantities of the related tris(2,4,4-trimethylpentyl)phosphine oxide ($\mathbf{L^2}$) and other trace impurities.[1-3]



$\mathbf{L^1}$H $\mathbf{L^2}$

Figure 1: Structures of $\mathbf{L^1}$H, the active phosphinic acid component of the CYANEX® 272 extractant formulation, and $\mathbf{L^2}$, the related phosphine oxide that is present as an impurity.

CYANEX®272's main commercial application involves the separation of Co(II) from Ni(II) in operations that usually involve prior removal of Fe(III) by precipitation as oxyhydroxides.[4-12] The deleterious environmental and economic impacts of incomplete removal of Fe(III) from base metal streams are well-documented,[4, 5] and consequently using CYANEX®272 to remove Fe(III) prior to Co and Ni recovery has been studied.[2, 13] Other applications such as the hydrometallurgical recovery of base and precious metals from secondary sources including waste electronic and electrical equipment (WEEE) in which iron is usually a major component of the pregnant leach solution[14] emphasize the importance of understanding the mechanism of Fe(III) uptake by CYANEX®272.

Several studies of the extraction of Fe(III), predominantly from sulfate media, define how the loading depends on variation on pH and on the concentrations of the extractant, Fe(III) and sulfate in the system.[2, 13, 15, 16] Slope analysis of loading plots has been used to determine the stoichiometry of the Fe(III)-containing species in the water-immiscible phase. The incorporation of HSO_4^- into the extracted species was supported by Biswas and Singha, and by Ahmed,[2, 13] but different compositions for the complex formed, [Fe(HSO_4)($\mathbf{L^1}$)$_2$] and [Fe(HSO_4)($\mathbf{L^1}$)$_2$($\mathbf{L^1}$H)$_2$] were suggested (i.e. a metal-to-ligand ratio of 1:2 and 1:4, respectively). Others have proposed that a 1:3 complex [Fe($\mathbf{L^1}$)$_3$] is formed in the organic phase.[15] The lack of consensus reflects the difficulty in determining the composition and structures of species formed in the organic solution phase.

In this paper, we apply additional techniques to probe the composition of the loaded organic phases. Proton-decoupled ^{31}P (^{31}P{^{1}H}) NMR spectroscopy was used to determine the extent of association of $\mathbf{L^1}$ or $\mathbf{L^1}$H with Fe(III), taking advantage of the paramagnetism of Fe(III), which causes suppression of signals from ^{31}P atoms that are directly bound to the metal ion. Monitoring the concentration of free $\mathbf{L^1}$H at various Fe-loading levels has allowed the $\mathbf{L^1}$:Fe(III)

stoichiometric ratio to be determined in the extracted species. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the concentrations of sulfur and iron and, hence, the stoichiometric ratio between SO_4^{2-} or HSO_4^- and Fe(III) in the extracted species. Electrospray ionisation mass spectrometry (ESI-MS) has been employed to investigate the chemical composition of Fe-containing species in the gas phase resulting from soft ionisation of components in the organic phases obtained in extraction experiments. DFT geometry optimisation calculations (gas phase) support the assignment of possible structures formed.

2. Methods

Solvents and reagents were used as received from Solvay, Sigma-Aldrich, Fisher Scientific UK, Alfa Aesar, Acros Organics or VWR International. Deionised water was obtained from a Milli-Q purification system.

General Extraction Procedures: Stock solutions containing 20 g L^{-1} iron in deionised water were prepared using $Fe_2(SO_4)_3$. In all extractions, the water-immiscible (organic) phases consisted of 5% (by volume) CYANEX®272 [an extractant consisting of 85% bis(2,4,4-trimethylpentyl)phosphinic acid, along with small quantities of tris(2,4,4-trimethylpentyl)phosphine oxide and other impurities] [1-3] in the commercial dearomatised kerosene diluent ISOPAR M (>99.5% aliphatic, ExxonMobil Chemical Company).

All volumes were measured with 1 mL and 5 mL Rainin edp3 automatic pipettes. Extraction mixtures consisted of 8 mL organic phase, 4 mL metal stock solution and 4 mL of a mixture of deionised water and either 1 M H_2SO_4 or 1 M NaOH stock solutions, the proportions of which were adjusted to vary the equilibrium pH after extraction, monitored using an Ionode IJ44 pH electrode. The mixtures were placed in vials, sealed, and subjected to vigorous magnetic stirring at a rate of approximately 900 rotations min^{-1} overnight at room temperature, conditions under which equilibrium is known to be achieved.[1] After separation, both the organic and aqueous phases were centrifuged for 15 min to remove entrained material. In some cases, to increase metal-loading beyond what could be attained using this method, loaded organic phases were subjected to the same procedure, using a fresh metal stock solution and deionised water. Organic phase iron and sulfur concentrations were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 5300DC spectrometer. Organic phase samples were diluted 1:400 in 1-methoxy-2-propanol and taken up by a peristaltic pump at a rate of 2.0 mL min^{-1} into a Gem Tip cross flow nebuliser and a Glass Cyclonic spray chamber. Argon plasma conditions were as follows: 1500 W RF forward power, argon gas flows of 20, 1.4 and 0.45 L min^{-1} for plasma, auxiliary and nebuliser flow, respectively. ICP-OES calibration standards for iron and sulfur were obtained from VWR International or Sigma-Aldrich.

A slightly different procedure was used to determine the pH-dependence of Fe-loading shown in Figure 2. Equilibrium distributions between organic (CYANEX® 272 ca. 10 vol%, i.e. 0.270 M phosphinic acid in ISOPAR M) and aqueous (ferric sulfate, 10 g L^{-1} iron in distilled water, concentration checked by ICP) phases as a function of pH were determined at 25°C by

contacting equal volumes (500 mL) in a jacketed reactor. The pH was adjusted by adding a known volume of either concentrated H_2SO_4 (96%) or 10 M NaOH solution. A contact time of 15 min was used after each pH adjustment. Aliquots were taken from each phase and filtered; the loaded organic was passed through phase separating paper (Whatman P/S 1) and the raffinate through qualitative (Whatman #1) paper. The loaded organic was stripped of metals by contacting with 200 g L^{-1} H_2SO_4 at an aqueous- to-organic phase ratio of five on a Burrell wrist-action shaker for 15 min at room temperature, and the phases were allowed to separate. The aqueous phases (strip liquor and raffinate) were analyzed for metal content by ICP-OES. The pH of raffinate solutions was measured using a Metrohm flat-bottomed pH-electrode (model 6.0256.100) and an Orion 920A pH meter with an automatic temperature correction probe initially calibrated at room temperature with pH 4.00 (potassium biphthalate) and pH 7.00 (potassium phosphate monobasic/NaOH) buffer solutions.

Metal-loading levels are reported as percentages, relative to the theoretical maximum quantity of metal that would be extracted by the phosphinic acid present in the organic phase, assuming a 3:1 stoichiometry of phosphinate to iron in the extracted complex, i.e., as in [Fe(**L^1**)$_3$].

NMR spectroscopy: $^{31}P\{^1H\}$ NMR spectra were recorded at 300 K on a Bruker PRO500 spectrometer as d^6-benzene solutions at a frequency of 202.40 MHz for ^{31}P and 500.12 MHz for ^1H. Spectra were analysed using the MestReNova software.[17]

Peak integrals were used to quantify the relative concentrations of species in the organic phase. Assuming **L^2** to be insignificantly involved in the extracted iron species below high loading levels, the ratio of the integrals of the peaks corresponding to unassociated **L^{1}H** and **L^2** was used to monitor the change in proportion of **L^1** associated to iron as % Fe loading increases. By comparison with the known absolute concentrations of unassociated **L^1** in the organic phase at 0% loading and of iron in the organic phase at 100% loading, the absolute rate of consumption of unassociated **L^1** versus iron uptake in the organic phase was calculated, and the stoichiometries of extracted species inferred.

Mass spectrometry: Electrospray ionisation mass spectra (ESI-MS) were recorded on a Bruker 12 T SolariX mass spectrometer with samples diluted into a 3:1 mixture of methanol and chloroform. Spectra were analysed using the Bruker Compass DataAnalysis software, with peaks assigned manually.

Computational modelling: All geometry optimisation calculations were performed using the Gaussian 09 software package.[18] The M06 functional was used in all calculations,[19] along with the LANL2DZ basis set and its associated pseudopotential for Fe and the 6-31+G* basis set for all other atoms.[20] Structures were considered optimised when the standard convergence criteria (maximum force of 4.5×10^{-4} Hartrees/Bohr on any atom, maximum RMS force of 3.0×10^{-4} over all atoms, maximum atomic displacement of 1.8×10^{-3} Bohr for any atom, and maximum RMS atomic displacement of 1.2×10^{-3} Bohr over all atoms) were reached.

3. Results

3.1 Extraction*:* The pH dependence of the uptake of iron by a CYANEX®272 solution (0.27 M) in ISOPAR M was determined (Figure 2).

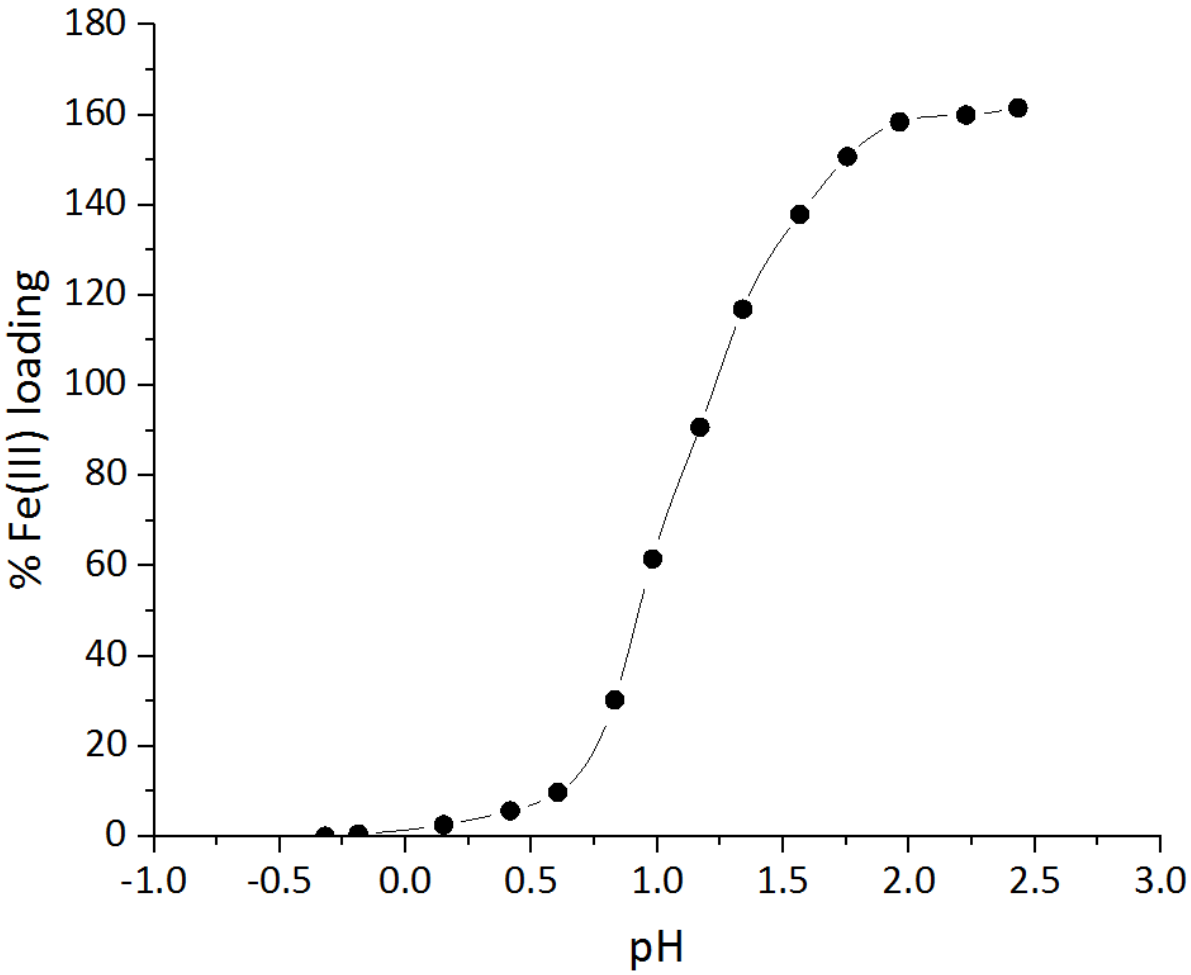


Figure 2: The pH dependence of Fe loading, by a 0.27 M solution of $\mathbf{L^1}$ in ISOPAR M. A loading of 100% is based on the formation of [Fe($\mathbf{L^1}$)$_3$] in the organic phase. The initial Fe^{3+} concentration in the aqueous phase was 0.81 M.

At equilibrium pH values > 1.2, Fe loading levels exceed those expected if the uptake of iron was entirely accounted for by formation of a complex of the form [Fe($\mathbf{L^1}$)$_3$] in the water-immiscible phase. This suggests that anionic species apart from $(\mathbf{L^1})^-$ must be involved in extraction, in order to create a charge-neutral assembly that could exist in the organic phase. This data is consistent with other studies that indicate that SO_4^{2-} or HSO_4^- uptake accompanies Fe-loading.[2, 13]

At equilibrium pH values greater than 2.5, extraction into the organic phase is disrupted by precipitation of an Fe(III)-containing complex. Higher percentage loadings than those shown in Figure 2 could be achieved through the use of a lower concentration of extractant (0.14 M as shown in Figure 3), giving up to 177% loading at the highest workable aqueous-phase pH values. This value does not correspond to any simple $\mathbf{L^1}$:Fe(III) stoichiometric ratio, which may imply that more than one Fe(III)-containing species is formed in the organic phase during Fe(III) extraction. However, the S-curve in Figure 2 has the classic shape with no plateaus or

points of inflection, and a constant molar ratio of Fe:S is observed across the Fe-loading range (see below), suggesting that only a single complex is formed.

As the Fe(III) stock solutions used in extraction experiments in this study were made by dissolution of iron(III) sulfate, they contain an abundance of SO_4^{2-} and/or HSO_4^- anions, which would seem likely candidates for any non-phosphinate anion involved in the extraction process. To test this, the sulfur content of the organic phase containing different Fe-loadings was measured using ICP-OES (Figure 3).

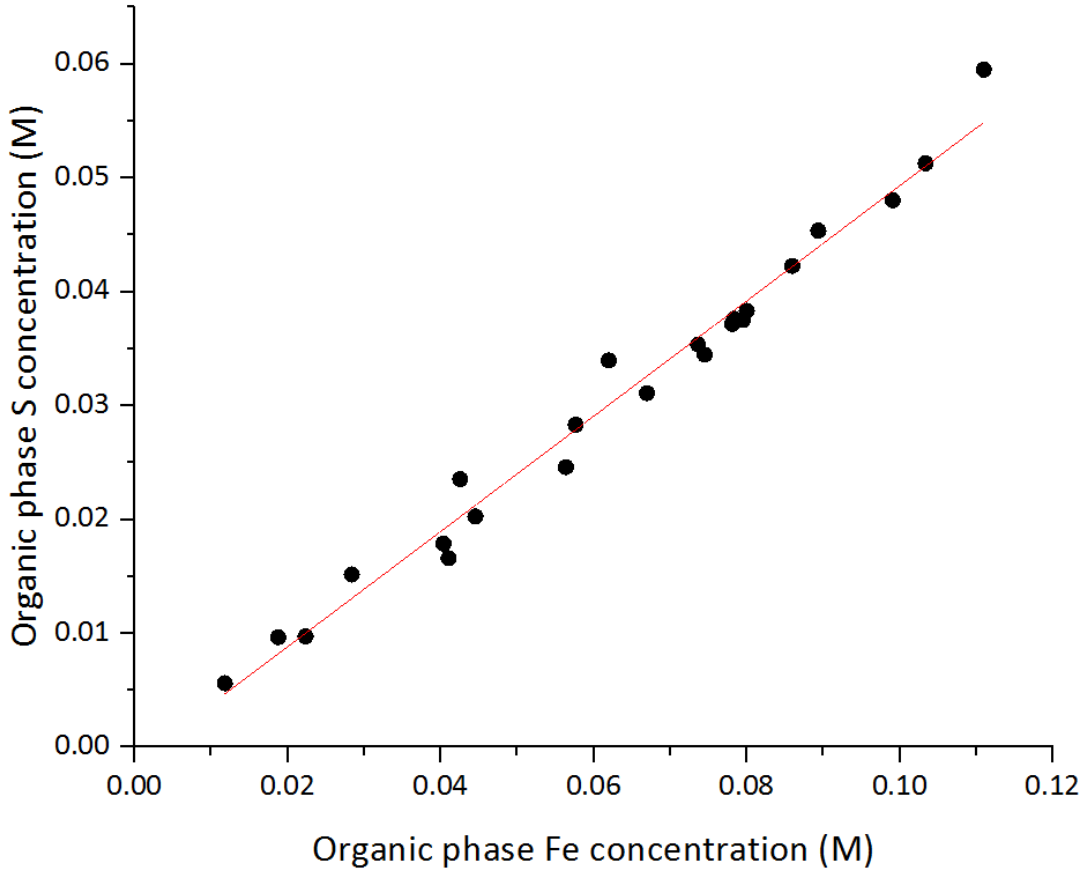


Figure 3: Variation of the sulfur concentration in a 0.14 M solution of CYANEX®272 in ISOPAR M with concentration of loaded iron. A calculated line of best fit is shown in red.

The sulfur concentration in the organic phase was found to increase linearly (with a best fit line of adjusted R-squared value 0.98) with uptake of Fe(III). The calculated line of best fit has a gradient of 0.51, indicating that 1 mole of SO_4^{2-} or HSO_4^- is extracted for every 2 moles of Fe. Although these findings support earlier observations by Biswas and Ahmed[2, 13] that a sulfur-containing species is always involved in the Fe(III) extraction mechanism, the 2:1 ratio of Fe to SO_4^{2-} or HSO_4^- we observe differs from the 1:2 and 1:4 ratios, respectively, that they report.

3.2 $^{31}P\{^1H\}$ NMR spectroscopy*:* The $^{31}P\{^1H\}$ NMR spectrum of a commercial sample of CYANEX®272 (see Figure 4a) contains an intense peak at 58 ppm corresponding to the phosphinic acid, $\mathbf{L^1}H$, and a less intense peak at 46 ppm arising from the phosphine oxide impurity $\mathbf{L^2}$.

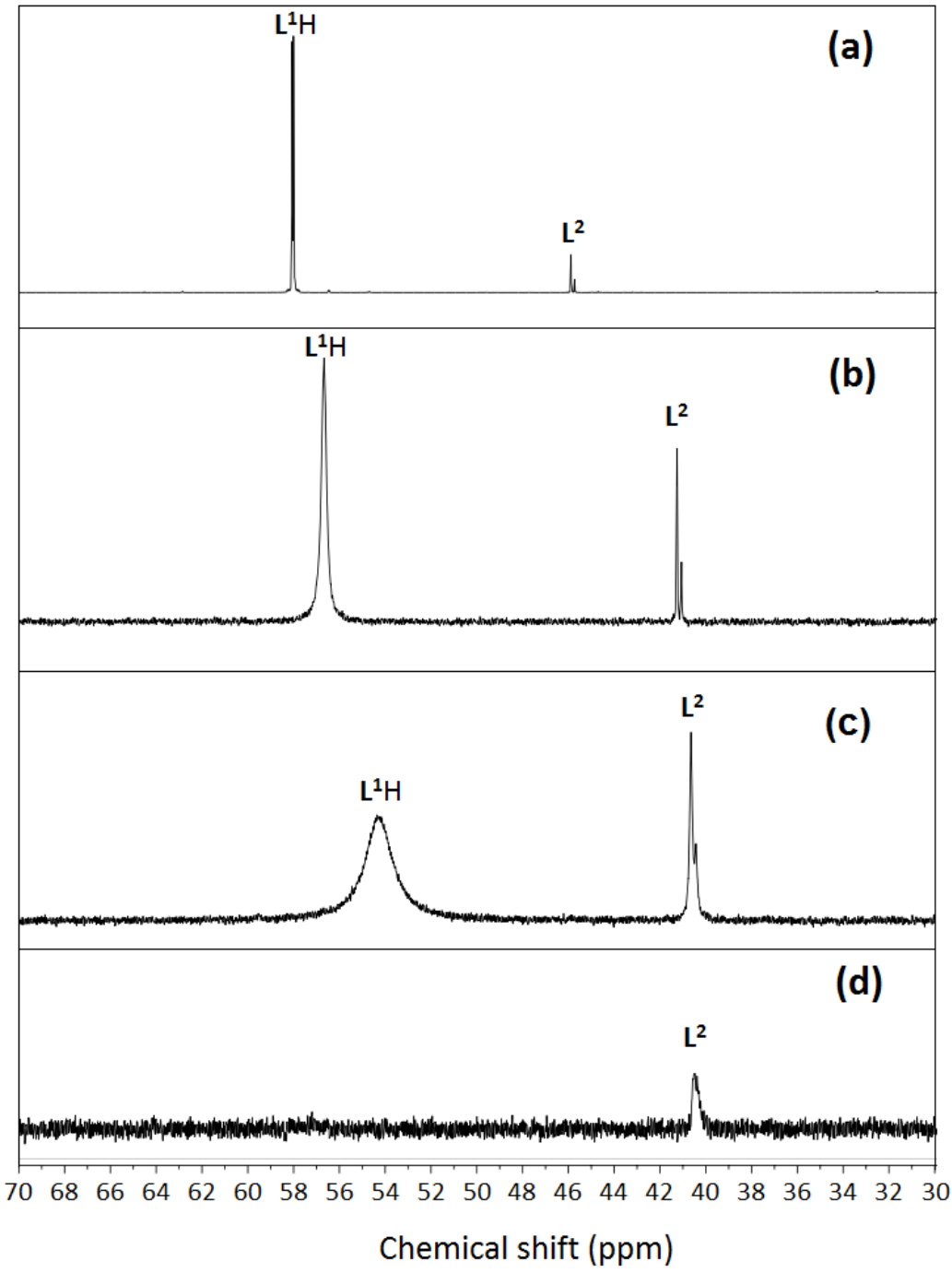


Figure 4: $^{31}P\{^{1}H\}$ NMR spectra of ISOPAR M solutions of CYANEX®272 with (a) no Fe loading and (b, c and d) Fe loading at levels of 32, 96 and 177% respectively, relative to the maximum loading level achievable through formation of a $[Fe(\mathbf{L^1})_3]$ complex alone.

The effects of three different levels of Fe loading are shown in spectra (b), (c) and (d) (Figure 4). Due to the paramagnetism of Fe(III), no $^{31}P\{^{1}H\}$ signals from $\mathbf{L^1}H$ or $(\mathbf{L^1})^-$ units in the inner coordination sphere of the metal, or closely associated with it, were seen between −1000 to +1000 ppm in spectra at any loading level. The $^{31}P\{^{1}H\}$ signal of $\mathbf{L^1}H$ becomes less intense as Fe loading increases, while no such decline in the intensity of the $\mathbf{L^2}$ signal is apparent until very high Fe loading levels, at which point the abundance of paramagnetic nuclei in the system appears to cause some degree of suppression of both signals. Assuming that incorporation of

$\mathbf{L^2}$ into Fe-containing complexes is negligible, and that suppression due to residual paramagnetism at high Fe-loading levels affects both peaks proportionately, then the amount of free $\mathbf{L^1}$H in the organic phase at different Fe-loadings can be derived from the ratio of the integral of the $\mathbf{L^1}$H ^{31}P signal to that of $\mathbf{L^2}$ (Figure 5).

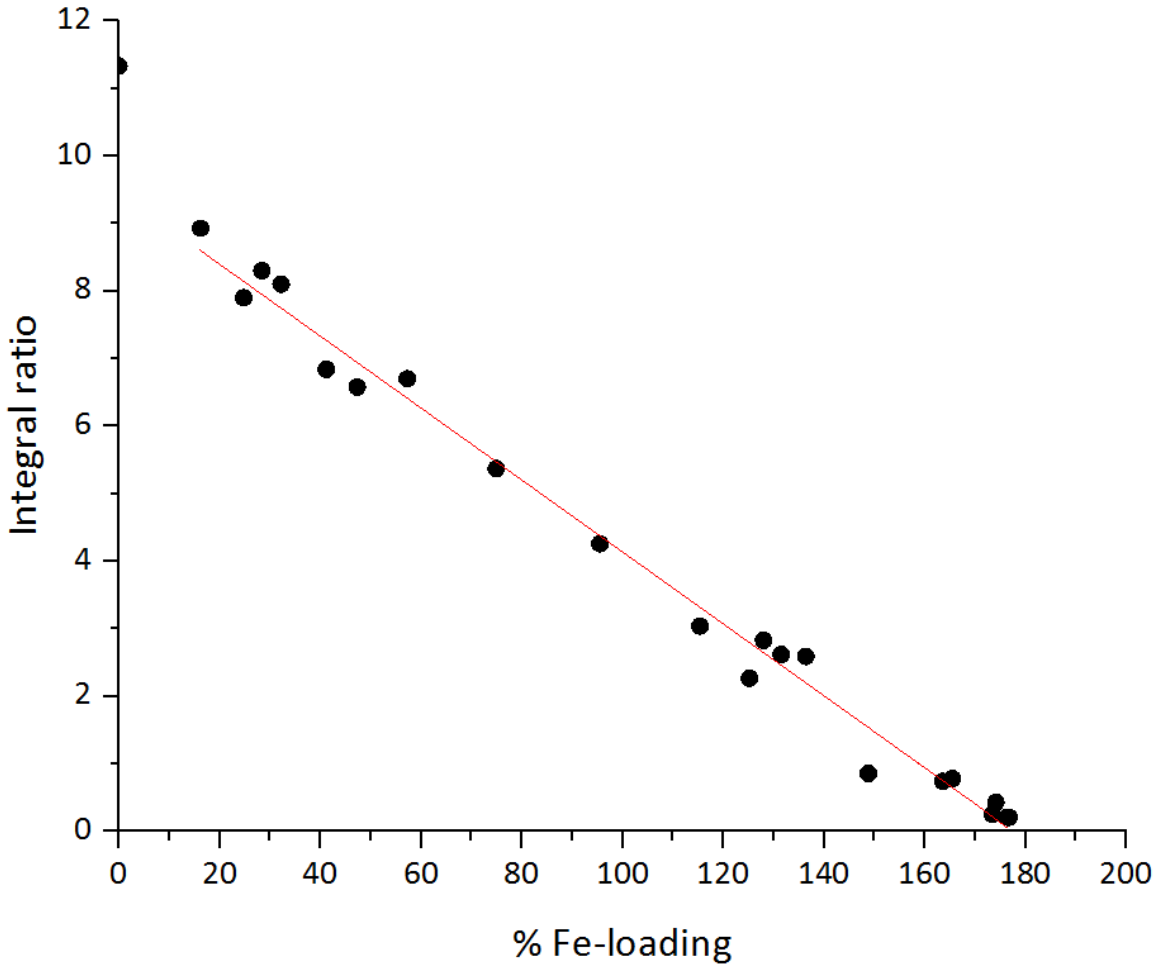


Figure 5. The ratio of the integrals of peaks $\mathbf{L^1}$H and $\mathbf{L^2}$ in ^{31}P{^{1}H} NMR spectra of ISOPAR M solutions of CYANEX®272 with different levels of Fe loading.

The linear dependence of loss of free $\mathbf{L^1}$H with Fe-loading (the best fit line yields an adjusted R-squared value of 0.98) suggests that a single Fe-containing species or species with a constant Fe:$\mathbf{L}^1$ stoichiometry is formed in the organic phase up to the maximum loading level observed of 177%. The best fit line intersects the x-axis (corresponding to an integral ratio of zero) at almost exactly this loading level, strongly suggesting that the observed limit of Fe(III) loading arises due to depletion of available $\mathbf{L^1}$H, rather than depletion of any other species. This behaviour contrasts markedly with the uptake of Co(II) by CYANEX®272, where the evidence points to the formation of polymeric species of significantly different molecular weights at different Co-loading levels, and as a consequence the viscosity varies considerably.[21-23] It also marks a further deviation from the Fe:2$\mathbf{L}^1$ or Fe:4$\mathbf{L}^1$ ratios reported for the extracted complex by Biswas and Ahmed.[2, 13]

3.3 Mass spectrometry and computational modelling:

The loading data and $^{31}P\{^{1}H\}$ NMR measurements indicate that the complex or complexes formed in the water-immiscible phase have the same Fe:**L**^{1} and Fe:SO_4^{2-} (or HSO_4^{-}) stoichiometric ratios across all Fe loadings. The chemical composition of these Fe(III) complexes was further studied by positive- and negative-ion ESI-MS (Figures 6a and 6b).

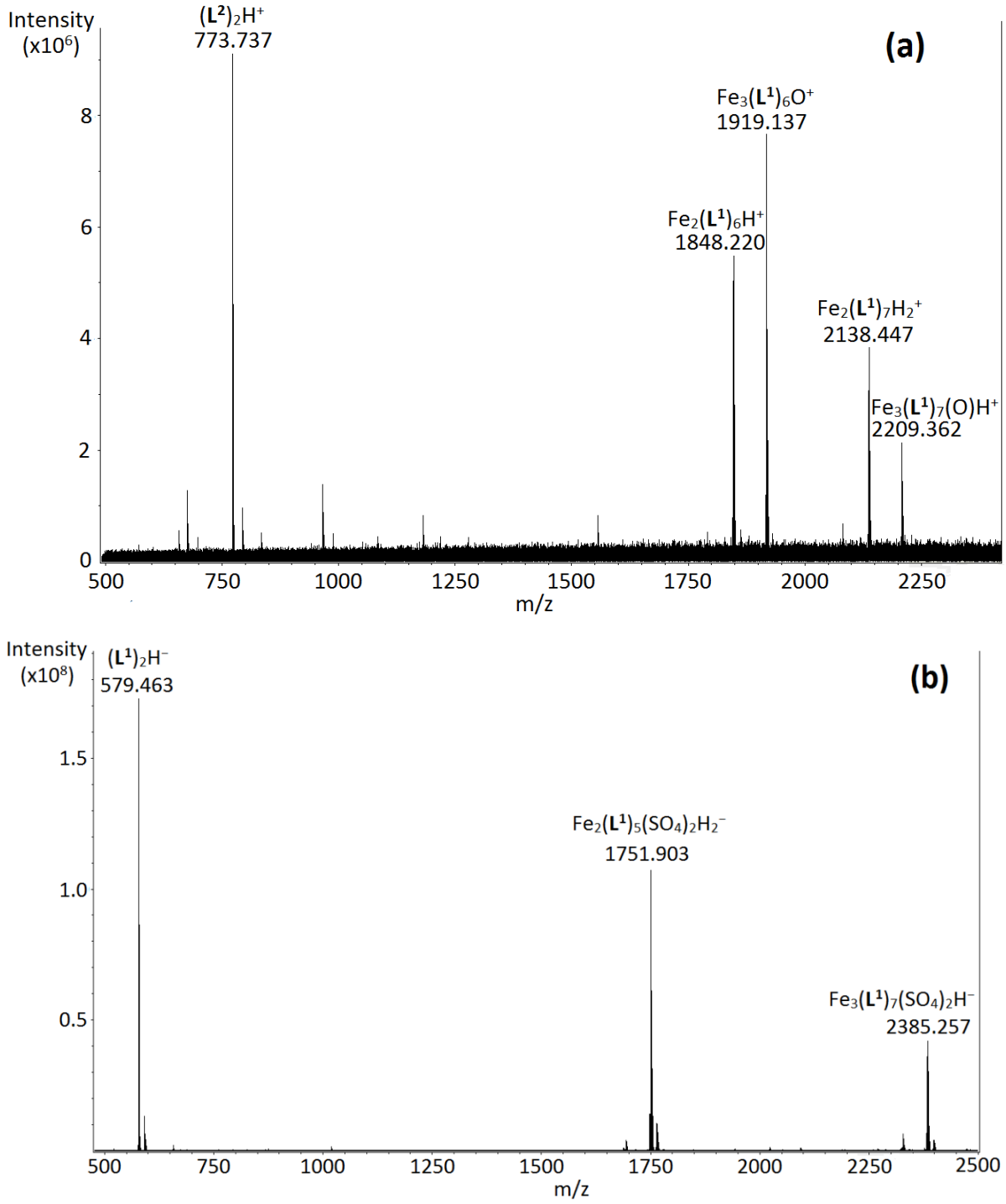


Figure 6: (a) Positive-ion and (b) negative-ion ESI mass spectra of a sample of CYANEX®272 at an Fe(III) loading level of 69%.

The peaks at *m/z* 773.737 in the positive-ion spectrum and at *m/z* 579.463 in the negative-ion spectrum can be assigned to species consisting solely of components of the CYANEX®272 formulation, the former a protonated dimer of the phosphine oxide molecules, $(\mathbf{L^2})_2H^+$, and the latter a protonated dimer of the phosphinate anions, $(\mathbf{L^1})_2H^-$.

Intense peaks at higher *m/z* values in the negative ion spectrum (Figure 6(b)) can all be assigned to Fe-containing species. The most intense, those at *m/z* 1751.903 and 2385.257, can be assigned to species containing either SO_4^{2-} or HSO_4^- ions, which is consistent with their co-extraction with iron (see Figure 3). The intense peak at *m/z* 1751.903 corresponds to an anion of formula $[Fe_2(\mathbf{L^1})_5(SO_4)_2H_2]^-$, which can be reasonably formulated as a dinuclear complex with terminal hydrogen-bonding sulfate and phosphinate units on each Fe(III) centre, creating favourable *pseudo*- eight-membered rings, along with three additional phosphinate units bridging the Fe(III) centres to create stable 6-coordinate geometries on each. An optimized geometry of this complex is shown in Figure 7(a). Alternative isomeric forms are possible with sulfate bridging the Fe atoms.

In contrast, in the positive-ion spectrum, no peaks can be assigned to structures containing *both* Fe and SO_4^{2-} or HSO_4^-. This finding is inconsistent with the analytical data on the loaded organic phase, which show a 2:1 molar ratio of Fe:S across the whole range of Fe-loading (Figure 3). The only rational explanation for the differences observed for the two types of mass spectrometry measurements is that the cations and ions that are created under the electrospray conditions will have different stabilities. Peaks at *m/z* 1848.220 and 2138.447 can be assigned as $[Fe_2(\mathbf{L^1})_6H]^+$ and $[Fe_2(\mathbf{L^1})_7H_2]^+$ respectively, while peaks at *m/z* 1919.137 and 2209.362 correspond to $[Fe_3(\mathbf{L^1})_6O]^+$ and $[Fe_2(\mathbf{L^1})_7(O)H]^+$ respectively. The former (and more intense) peak can be visualised as a trinuclear complex with the three Fe(III) centres connected by a central oxo anion and pairs of bridging phosphinate units, an optimized geometry shown in Figure 7(b). Complexes containing three iron atoms bridged by a single oxo ion have been studied extensively,[24] and an example having an additional phosphinate ligand bridging iron centres has also been reported.[25]

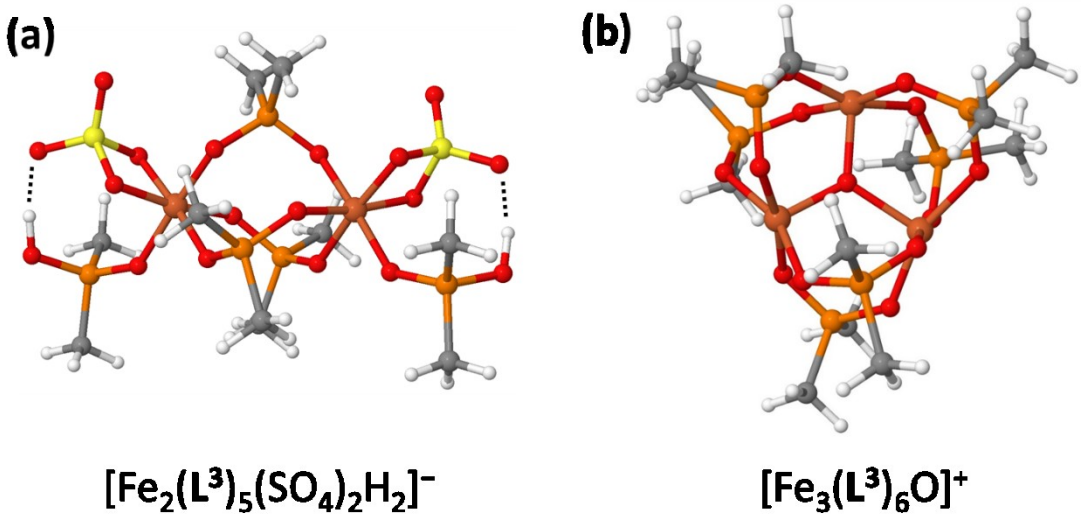


Figure 7: Energy-minimized geometries of possible structures of (a) $[Fe_2(\mathbf{L^3})_5(SO_4)_2H_2]^-$, the species responsible for the peak at *m/z* 1751.903 in the negative-ion ESI mass spectrum shown in

Figure 6(b), and (b) $[Fe_3(\mathbf{L^3})_6O]^+$, the species responsible for the peak at *m/z* 1919.137 in the positive-ion ESI mass spectrum shown in Figure 6(a).

It is noteworthy that no peaks corresponding to mononuclear Fe-species are observed in either positive or negative ion spectra, suggesting that the extraction of Fe(III) by CYANEX® 272 operates differently from other base metals in that it always involves the formation of polynuclear complexes.

4. Conclusions

Some, but not all, of the results of the analytical and structural techniques applied to identify the nature of the iron complexes formed by the extractant CYANEX®272 in this work are consistent with previous reports.[2, 13] It is possible that the differences that have been observed are a consequence of the conditions (e.g., the concentration of $Fe_2(SO_4)_3$, *ca.* 0.08 M in the aqueous phase) differing from those applied previously. In the current work, the Fe-concentrations used mirrored those of studies of Co(II) and Zn(II) extraction, which demonstrated that polymeric complexes were formed and which accounts for the high viscosity observed at high Co(II) and Zn(II) loading.[21] Formation of similar complexes by Fe(III) could present problems in systems where recovery of base metals is accompanied by Fe(III)-uptake that is not readily acid-stripped. However, in accordance with other studies,[2, 13, 15, 16] there is no evidence for increased viscosity with Fe-uptake, even at the 177% loading level achieved in this study by undertaking multiple contacts with an $Fe_2(SO_4)_3$ solution. A 100% loading is based on the 3:1 stoichiometric ratio between the phosphinate $\mathbf{L^{1-}}$ and Fe(III) in the complex $[Fe(\mathbf{L^1})_3]$. Like others,[2, 13] we find no evidence for the formation of this or oligomeric analogues $[Fe(\mathbf{L^1})_3]_n$.

$^{31}P\{^1H\}$ NMR spectra of Fe-loaded ISOPAR M solutions indicate that consumption of unassociated $\mathbf{L^1}H$ proceeds almost linearly with increasing Fe-uptake, suggesting that the mechanism of Fe(III) extraction remains the same across all loading levels. The dependence of consumption of unassociated $\mathbf{L^1}H$ on Fe-uptake implies a molar ratio around 1.4:1 of $\mathbf{L^1}$ to Fe in the extracted species. The maximum loading of Fe occurs at the point at which all $\mathbf{L^1}H$ in the organic phase is present in an Fe(III) complex.

Direct analysis of the sulfur content in the water-immiscible phase indicates that HSO_4^- or SO_4^{2-} are part of the iron complex(es) formed. In our work the Fe:S atomic ratio was found to be close to 2:1 across a wide range of Fe-uptake levels. The incorporation of hydrogensulfate or sulfate ions into Fe(III) complexes provides a very plausible explanation for the loading exceeding the 100% limit if only $(\mathbf{L^1})^-$ phosphinate anions are used to create charge-neutral, hydrocarbon-soluble assemblies. This result differs from that of Biswas *et al.,* who concluded that the Fe:S ratio was 1:1, from studies of the dependence of Fe-loading on sulfate concentration in the aqueous phase.[2] It is conceivable that the disparity arises due to differences in concentrations of available iron (see above). If processes are to be developed for the removal of iron from aqueous solutions under varying conditions, it will be of great interest to investigate any differences in the extraction mechanisms further.

Unlike other recently reported work,[21, 26] electrospray ionisation mass spectra of Fe(III)-loaded organic phases provide ambiguous results in identifying the major species present in the condensed phase. The species identified in positive- and negative-ion spectra are very different. The negative-ion spectra contain species more closely related to those suggested by the other techniques used in this work. No mononuclear Fe complexes are observed, and all others contain SO_4^{2-} or HSO_4^- anions (in accordance with ICP-OES measurements). Species containing oxy, O^{2-}, or hydroxyl, OH^-, anions are present in the positive-ion spectra and probably use these to bridge iron centres as observed in many complexes described previously.[24, 27] In the Fe(III)/CYANEX® 272 system, facile rearrangement of complexes appear to be a feature of the ionisation processes.

In a more general context, as the extractions in this work were conducted under very similar conditions to those used earlier[21] on Co(II) and Zn(II) uptake by CYANEX® 272, they draw attention to remarkable differences in loading mechanisms. Unlike for Co and Zn, there is no evidence in Fe-extraction for the formation of complexes that contain a pseudochelate ring (Figure 8a). In all extractions of M^{2+} transition metal cations, the formation of 8-membered rings predominates at low metal loadings.[6, 7] Such pseudochelate units are also found in solid-state structures of phosphinate complexes of M^{2+} metals, but not in those of M^{3+} metals.[28]

In contrast to Co(II) and Zn(II) extraction,[21] uptake of Fe(III) from sulfate solutions is always accompanied by the incorporation of sulfate into the assembly formed in the organic phase. Unlike the complexes formed by Co(II) and Zn(II) in extractions by CYANEX® 272, there is no evidence that Fe(III) forms polymeric complexes with high molecular weight and viscous solutions at high metal loading. One similarity does exist in the uptake of Co(II), Zn(II) and Fe(III) by CYANEX® 272; there is no evidence for the phosphinate forming 4-membered chelate rings (Figure 8b) of the types suggested in some earlier papers on Fe(III) extraction.[2,15,16] Recently DFT calculations confirmed that in the gas phase the formation of the Co(II) complexes $[Co(\mathbf{L}^2)_2]$ with bidentate dimethyl phosphinate is thermodynamically unfavourable in the presence of $\mathbf{L}^2H$ with respect to the 8-membered pseudo chelate complex $[Co(\mathbf{L}^2.\mathbf{L}^2H)_2]$.[21]

At high M(II)-loadings the phosphinate most likely assumes a bridging mode (Figure 8c). This mode is by far the most common found in solid-state metal phosphinate structures.[28] If sulfate is involved in a bridging mode (Figure 8d) in dinuclear Fe(III) complexes it would account for the 2:1 Fe-to-sulfate stoichiometry observed in extractions in this work and the observation that there is no increase in viscosity (i.e. formation of polymeric structures) at high Fe-loadings.

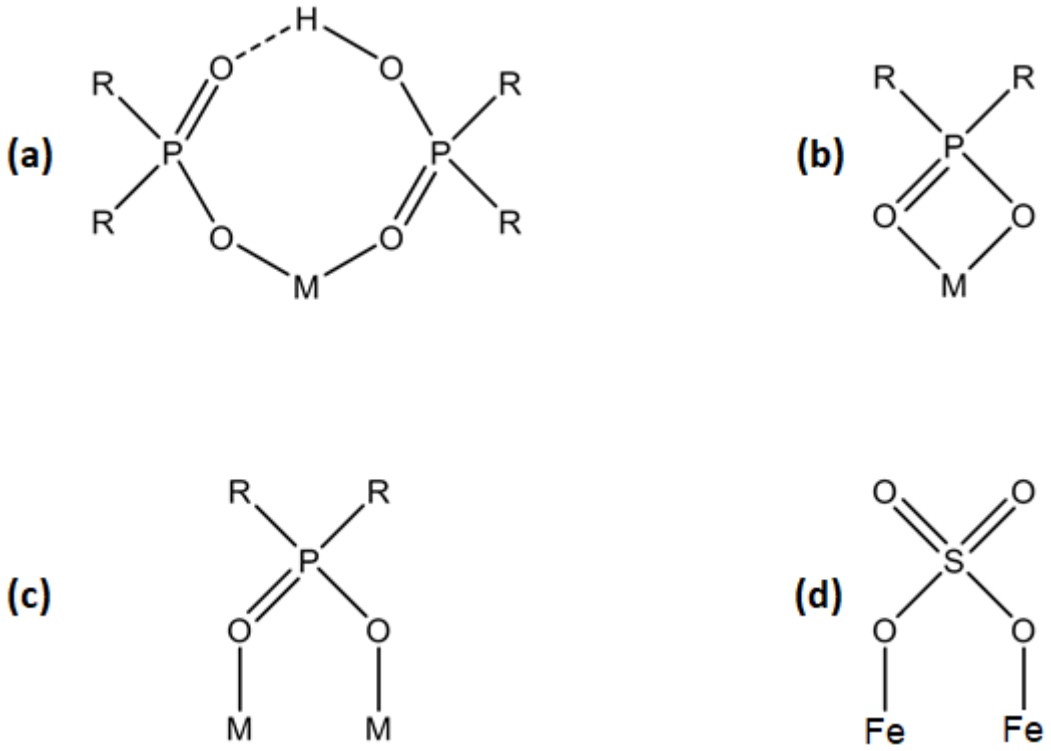


Figure 8: (a) The 8-membered pseudochelate ring in phosphinate complexes $[M(\mathbf{L}.\mathbf{L}H)_n]$, (b) the theoretical 4-membered chelate ring in $[M(\mathbf{L})_n]$, (c) the most common binding mode observed[28] in solid-state phosphinate complexes {μ_1-bridging, $[M(\mathbf{L})M]^{n+}$}, and (d) a comparable μ_1-bridging mode, $[Fe(SO_4)Fe]^{n+}$, possibly present in extracts from Fe(III) sulfate solutions.

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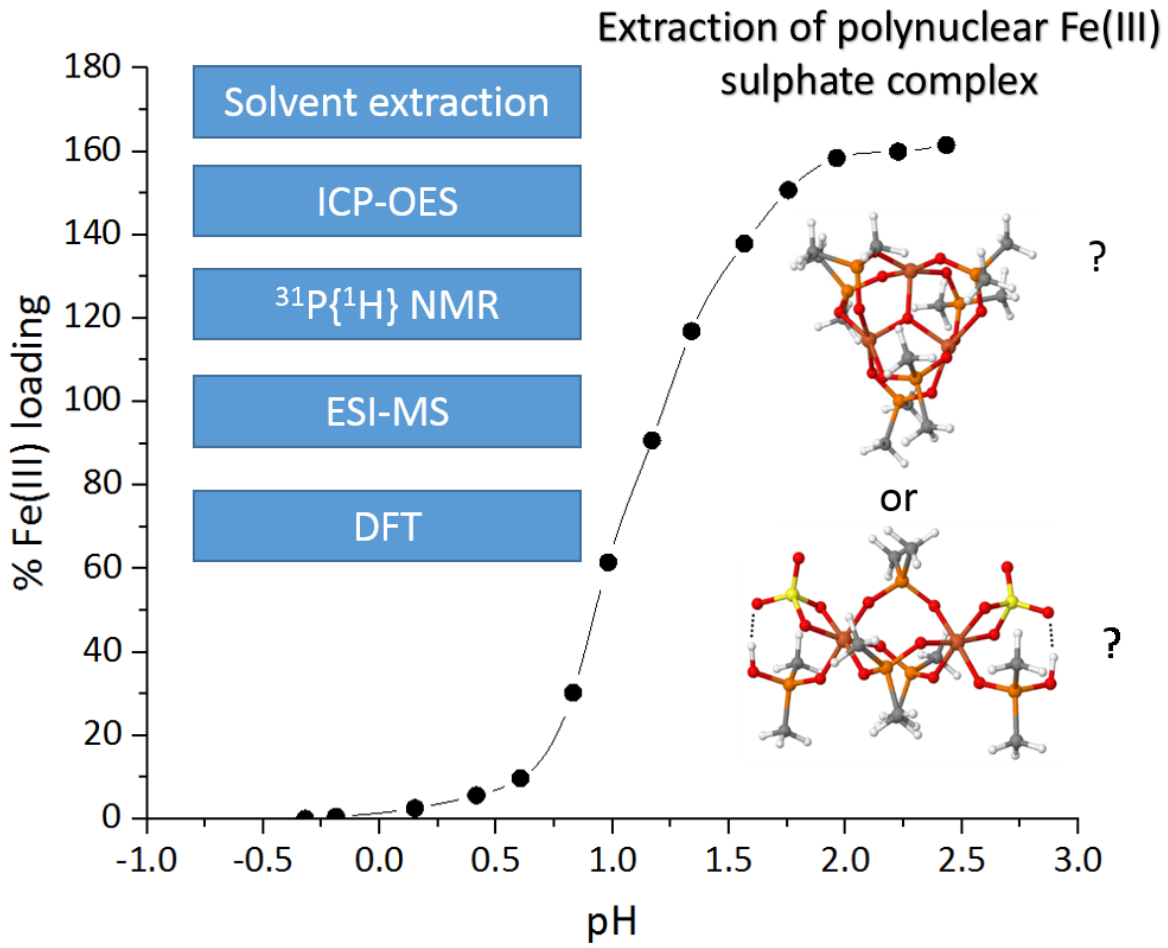
Graphical Abstract



Research Highlights:

- Study of Fe(III) uptake from sulfate solutions by CYANEX®272 using solvent extraction, $^{31}P\{^{1}H\}$ NMR spectroscopy, ESI-MS and DFT calculations, to understand the nature of iron complexes formed.
- Some, but not all, of our findings are consistent with previous literature reports, which we attribute to a change in extractant mechanism with Fe(III) concentration.
- Findings indicate that at ca. 0.08 M Fe concentration sulfate or hydrogen sulfate ions are co-extracted in a 2:1 (Fe:S) molar ratio with Fe(III) across the whole of the Fe-loading range.
- Limiting factor in Fe-loading is the availability of uncomplexed CYANEX®272.
- In contrast to Co(II) and Zn(II) extraction by CYANEX®272, there is no evidence for the formation of polymeric Fe(III) complexes and highly viscous solutions at high

metal loadings. Extracted species is most likely a polynuclear Fe(III) sulphate complex.